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Fast chemical separations and laser mass spectrometry – tools for nuclear research

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Fast chemical methods /
Discontinuous and continuous separation procedures /
Investigation of short-lived nuclei /
Resonance ionization mass spectrometry (RIMS) /
Ultra trace analysis of plutonium and neptunium /
First ionization potentials of the actinides and technetium

Summary. Fast chemical separation procedures applied in nuclear research require dedicated experimental techniques. Rapid discontinuous separation procedures are illustrated by an example to isolate technetium from fission products. The use of a gas jet and its combination with a thermochromatographic separation and with the continuous solvent extraction technique SISAK is described and examples are given for the investigation of short-lived fission products. The potential of resonance ionization mass spectrometry (RIMS) as a highly sensitive technique using different experimental systems is outlined for ultra trace analysis of long-lived plutonium and neptunium isotopes, including isotope ratio measurements of the plutonium isotopes. In addition, the precise determination of the first ionization potentials (IP) of ten actinide elements up to einsteinium and of technetium carried out by using the photoionization threshold method and requiring sample sizes of $\sim 10^{12}$ atoms is presented.

1. Introduction

Chemical separation procedures have played an important role in the identification and investigation of radioactive isotopes since the discovery of radioactivity [1]. Among others, the application of chemical procedures has led to the discovery of the first radioactive elements in nature, polonium and radium [2, 3], the artificial radioactivity [4], the nuclear fission process [5], the identification of the first synthetic element, technetium [6], and of the first transuranium element, neptunium [7]. Radiochemical separations enable to unravel very effective mixtures of radioactive species and to assign atomic numbers. The demands on the individual chemical procedures to be used depend considerably on the particular case. For the identification of a nuclide through its characteristic radiation, a rather unselective chemical separation technique may be sufficient, whereas for detailed decay studies very selective methods are required.

The investigation of the chemical properties of the transactinide elements has been a great challenge because strong relativistic effects were predicted for those elements [8]. Those effects may lead to deviations from the periodicity of the chemical properties based on linear extrapolations from the lighter homologues in the Periodic Table of the elements. Regarding the chemical separation of the heaviest elements, which are generated artificially by fusion experiments, the one-atom-at-a-time production must be considered. In order to exclude that a chemical behaviour of individual atoms differs from those of bulk amounts, the separation step has to be repeated very often with the consequence to use multistep procedures.

In the last years special attention has been paid to the study of nuclides with half-lives in the range of seconds to minutes, requiring particularly fast chemical procedures. Already Hahn and Strassmann [9] used fast procedures and discovered nuclides with half-lives down to less than one minute. Since that time brilliant experimental techniques such as computer-controlled automated systems have been developed for nuclear research on short-lived isotopes.

In general, there are two main approaches to fast radiochemical separations: the batchwise discontinuous and the continuous operation. In discontinuous procedures a nuclide is produced, chemically separated and measured sequentially. In continuous procedures a target is permanently irradiated and extraction of the produced species from the target, chemical separation and counting are performed online. Several review articles on fast radiochemical separations and their applications to nuclear research have been published, see *e.g.* [10–15].

In this paper a survey of some experimental techniques developed to perform fast chemical separations is given with a special emphasis on the work carried out at the Institut für Kernchemie in Mainz. Since a TRIGA pulsing nuclear reactor is the major facility of this institute the application of rapid chemical separations is demonstrated for the study of neutron-rich nuclei produced in neutron-induced fission of fissile materials like U-235, Pu-239 or Cf-249. Most of the procedures are based on solvent extraction, gas-phase chemistry, or thermochromatography. These techniques are,

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however, also applicable to other regions of the Periodic Table, either directly or after slight modifications. Recently fast chemical separation methods have predominantly been used for studies of the chemical behaviour of the transactinide elements. More details on this topic are presented in another article in this special issue [16].

Laser mass spectrometry used as a versatile and sensitive tool for ultra trace analysis and fundamental atomic spectroscopy on radioactive isotopes is based on the stepwise optical excitation of atoms by resonant absorption of photons, delivered from tunable laser sources, followed by photo-ionization of the excited species and the subsequent detection of the resulting ions in a conventional mass spectrometer [17, 18]. This technique called resonance ionization mass spectrometry (RIMS) offers various advantages which can be applied most usefully for nuclear research studies:

- Good overall efficiency and thus excellent sensitivity is obtained as a result of the large cross sections of the optical excitation and ionization processes combined with the high transmission of the mass spectrometer and an efficient particle detection which makes this technique independent of the half-life of an individual radioisotope.
- Almost complete suppression of atomic or molecular isobaric interferences is achieved due to the uniqueness of the optical resonance lines of each element.
- High isotopic selectivity results from the isotopic shifts in the optical excitation and the mass separation process.

These qualities make RIMS an exceptionally versatile method for ultra trace analysis and isotope measurements of long-lived radioisotopes. This technique is also used for the determination of rare isotopes, solid state surface analysis, detection of explosives and chemical warfare agents as well as for fundamental investigations in quantum optical studies and the precise investigation of the atomic structure, in particular the determination of the first ionization potential of radioactive elements [17–22].

In this contribution the focus will be put on ultra trace analysis and isotope ratio measurements of the long-lived isotopes of plutonium and neptunium. Trace amounts of these elements are mainly found in the environment as a result of nuclear weapons tests, accidents and release from nuclear facilities. The isotopic composition of the plutonium contamination is related to its origin; *i.e.*, the isotope signature should be measurable with high accuracy in order to allow a statement on the source.

The extreme sensitivity and selectivity of RIMS is a prerequisite for migration studies of plutonium and neptunium in the context of long time storage of nuclear waste and low level surveillance of the environment. The long-lived isotopes of both elements determine predominantly the radiotoxicity of spent nuclear fuel after the decay of the fission products and therefore extensive investigations on their geochemical properties and migration behaviour in different host materials in the concentration range $\leq 10^{-10}$ mol/L, as expected in the aquifer in case of a leakage in a nuclear waste repository, are necessary.

Alpha-spectroscopy is not well suited for sensitive analytical measurements of the important isotopes of plutonium and neptunium due to the relatively long half-lives of these isotopes and the difficulty to distinguish between certain isotopes emitting radiation of similar energy like Pu-239 and Pu-240. Inductively coupled plasma mass spectrometry may suffer from isobaric interferences and tailing [23–26] which is also true for thermal ionization mass spectrometry [27]. An alternative, very sensitive and selective detection method is accelerator mass spectrometry (AMS) which provides isotope selectivities up to 10^{15} and detection limits down to 10^4 atoms [28] with the disadvantage of relatively high experimental expenses. However, AMS and RIMS, the latter has been in use now for more than 35 years in the isotope-selective ultra trace analysis of long-lived radioisotopes [17–21, 29–33], are one element techniques and not suitable for multi-element analysis.

The first ionization potential (IP) of an element is a fundamental physical and chemical property which governs chemical bonding. Its precise determination enables the identification of systematic trends in binding energies from element to element and the interpretation of atomic spectra. For the heaviest elements the ionization potentials allow a comparison with the predictions of multi-configuration Dirac–Fock calculations [34, 35] and a better understanding of relativistic effects as a consequence of the relativistic mass increase of the inner electrons [36] leading to deviations from the regularities of the periodic system of elements.

The first ionization potentials of the lighter actinides were determined by surface ionization and electron impact [37, 38] as well as from thermochemical data and appropriate Born–Haber cycles [39]. From extrapolated spectral properties [40, 41] the ionization potentials for all actinide elements up to einsteinium could be calculated. An alternative method is an analogy consideration between lanthanides and actinides with the semi-empirical Slater–Condon method and *ab initio* Hartree–Fock calculations [42]. A breakthrough with respect to precision was achieved with multistep laser ionization techniques [32, 43–45] which were applied for the determination of the first ionization potentials of Th, U, Np, and Pu studying the convergence of long Rydberg series. For the interpretation of such measurements a large amount of data and thus also of material was required; *i.e.*, as much as 2 g of Pu-239 were needed for the accurate measurement of the ionization potential of plutonium [45] which shows the limit of this technique for the heavier actinides.

Applying RIMS in the presence of different external static electric fields, the first ionization potentials of ten actinide elements [22] could be determined either for the first time (Ac, Am, Cm, Bk, Cf, Es) or remeasured (Th, U, Np, Pu) by extrapolation of the photoionization thresholds obtained with various field strengths to zero field strength. Here samples of only $\leq 10^{12}$ atoms (≈ 400 pg) are required. Very recently with an improved apparatus the exact IP of technetium could be determined precisely by evaluating Rydberg convergences [46] for which a total amount of 1 μg of the long-lived isotope Tc-99g was used.

2. Experimental techniques

2.1 Fast chemical separations

2.1.1 Discontinuous separation procedures

Most of the discontinuous separations are performed from aqueous solutions by transferring either the desired or the

accompanying elements into a second phase which can be solid, liquid or gaseous. Whether such a method can be applied on a short time scale depends on the chemical reactions involved and the techniques for fast phase separations. The transfer into a solid phase can be accelerated by replacing the precipitation step by a heterogeneous exchange reaction [47]. In solvent extraction the separation of the two phases – as a rule – is the slowest step and not the transfer from one liquid phase into another. This can be accelerated by using quasi-solid solvents prepared by fixing the organic phase on fine grained plastic carriers through which the solution is filtered quickly [48]. The volatilization of hydrides by nascent hydrogen [49] is an example for the rapid transport from a liquid into a gaseous phase with high yields.

Normally a combination of several separation steps is necessary for the selective isolation of an element. Separations on a time scale of seconds must be operated automatically by, *e.g.*, an electronic programmer which controls the whole sequence.

An example of such a discontinuous procedure is the separation of technetium from fission product mixtures [50] illustrated in Fig. 1. The main steps are: (1) removal of the halogens by exchange with silver chloride. (2) Solvent extraction of the pertechnetate ion into a solution of tetraphenylarsonium chloride sorbed on a fine-grained carrier. (3) Back extraction of the pertechnetate from this solvent and its coprecipitation with tetraphenylarsonium perrhenate. (4) Filtration and projection of the precipitate to the detector. This rather complicated procedure with programmer-controlled operation is finished after 7.5 s. The electronic programmer delivers signals at predetermined times which opens valves to deliver, *i.e.*, pressure to small pistons moving Teflon stopcocks.

With a less complicated apparatus it was possible to separate niobium from fission products within 2.2 s [51] involving the removal of bromine and iodine by exchange on a silver chloride layer and sorption of niobium on a fibreglass filter from strong nitric acid solution. Again the time steps are initiated by opening and closing stopcocks operated pneumatically at times determined by an electronic programmer. With this separation procedure in combination with high resolution γ-ray spectroscopy the neutron-rich niobium isotopes up to 0.8 s Nb-104 could be studied in detail [51].

Aqueous chemistry of the lighter transactinide elements has been performed thus far predominantly in a discontinuous manner either with the Automated Rapid Chemistry Apparatus ARCA II [52] or with the Automated Ion exchange separation apparatus coupled with the Detection system for Alpha spectroscopy AIDA [53]. Both systems are computer-controlled and used for fast, repetitive high per-

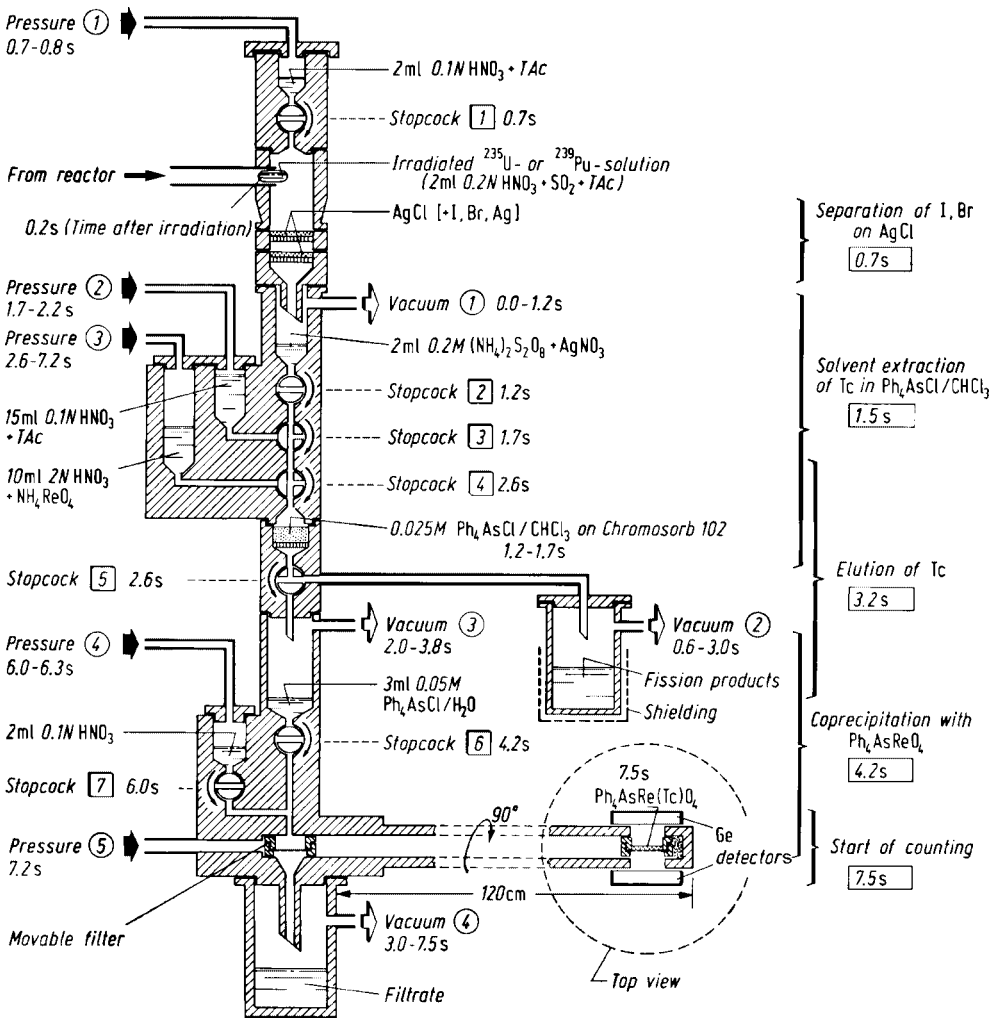

Fig. 1. Apparatus and time schedule for the fast separation of technetium from fission products [50]. At the right-hand side the time for each separation step is indicated.

formance chromatographic separations in combination with a gas jet transport system.

Fast chemical separations with ARCA II were applied for the transactinide elements 104, rutherfordium, 105, dubnium, and 106, seaborgium [13, 14] while AIDA has so far mainly been used for detailed studies of rutherfordium and dubnium [13, 14].

2.1.2 Continuous separation procedures

Continuous separation procedures are predominantly used nowadays for detailed studies of short-lived nuclides. In such on-line methods the target is permanently exposed to a beam of neutrons or heavy ion particles and the reaction products from the target are continuously transported to the separation apparatus. For the transport of the nuclear products one has to consider volatile or non-volatile species. Whereas the former can directly be removed with a gas system, the latter are transported in a gas jet system.

The gas jet technique [54, 55] uses mostly helium or nitrogen as carrier gases and KCl often as cluster material, especially for separations in the aqueous phase whereas for separations in the gas phase MoO_3 or carbon have found widespread application [56]. The recoil products attached to the clusters with 50–200 nm diameter are transported through a capillary of 1–2 mm diameter and a length of up to some tens of metres to the chemistry system with yields of more than 60% and hold-up times of a few seconds.

The combination of a gas jet system with thermochromatography applying reactive agents to form volatile species is one approach for continuous separations of short-lived nuclei. One example, namely the separation of the fission product chlorides [57] in a quartz column filled with quartz powder is outlined in Fig. 2. The reaction products of neutron-induced fission of U-235 were transported to the quartz column by a nitrogen/KCl jet. Along the column a temperature gradient from 900 to 0 °C was maintained. Conversion of the reaction products into volatile species was achieved by stopping the clusters in a quartz wool plug located at the entrance of the column and kept at 900 °C and feeding chlorine as a reactive gas into the column.

Fast gas phase techniques have also been used for the separation of rutherfordium, dubnium, seaborgium, and bohrium and the determination of their adsorption enthalpies and entropies [13, 15]. The compounds studied were the volatile chlorides, bromides and oxohalides of these lighter 6d-elements. The typical temperatures at which the chromatographic investigations were performed ranged from 150 to 400 °C. The high volatility of hassium tetroxide required cryo-chromatographic set ups [58] for the chemical studies of element 108 [13].

Continuous operation of fast solvent extraction procedures became possible with high speed centrifuges for rapid phase separation [59]. Over the years the centrifuge system has been improved so that with the SISAK 3 technique [60, 61] nuclides with half-lives down to ~ 1 s can be separated from complex fission product mixtures and investigated. Fig. 3 shows as an example the on-line isolation of short-lived technetium isotopes [62]. For the production of these isotopes a Cf-249 target was irradiated at the Mainz TRIGA reactor with thermal neutrons and the recoil fission products were transported from the target position by a nitrogen/KCl gas jet to the separation system SISAK 3. The KCl-clusters with the attached fission products were dissolved in diluted sulfuric acid containing an oxidizing agent in a static mixer, and afterwards N_2 and the fission noble gases were removed from the liquid in a degassing centrifuge. In the next step technetium was extracted into tetraphenylarsonium chloride dissolved in chloroform. After the extraction the organic phase was pumped to a measuring cell placed in front of Ge-detectors. The overall hold-up time from production to counting was determined to be 2.5 s.

The chemistry of element 104, Rf, was studied with SISAK 3 [63] in Berkeley applying 4.1 s Rf-257 produced *via* the ^{208}Pb(^{50}Ti, 1*n*) reaction. With the Berkeley Gas-Filled Separator a preseparation of Rf-257 occurred and subsequently Rf-257 was transported by means of a gas jet

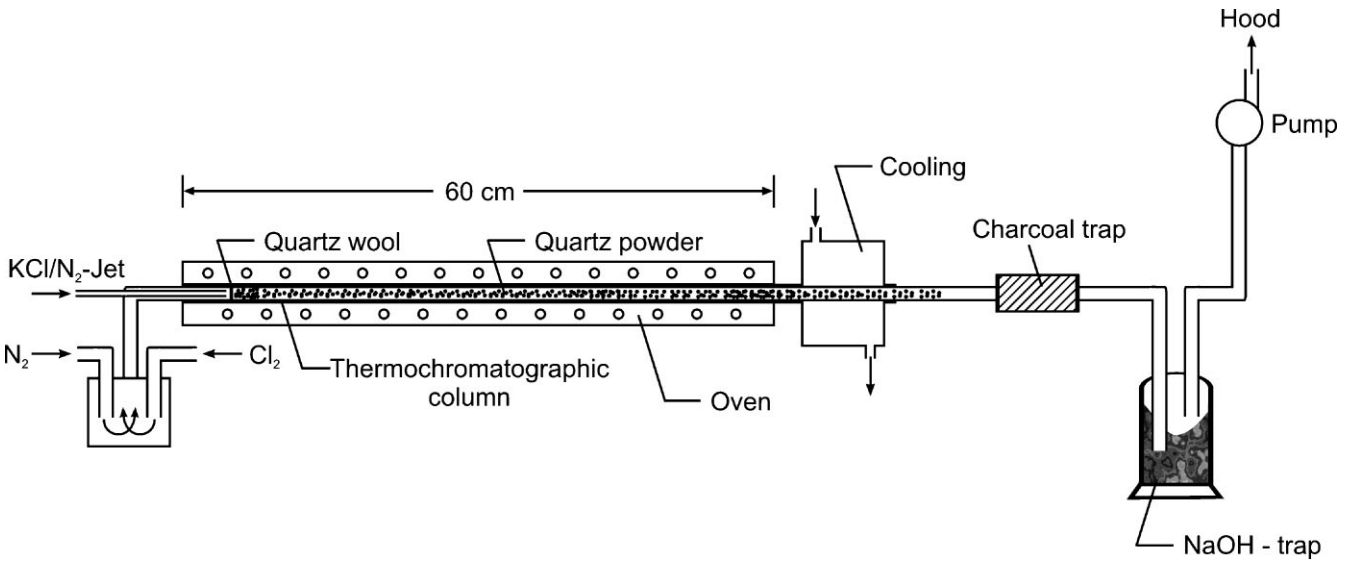

Fig. 2. Set up for continuous separation of fission product chlorides by combining a gas jet transport system with a thermochromatographic column [57].

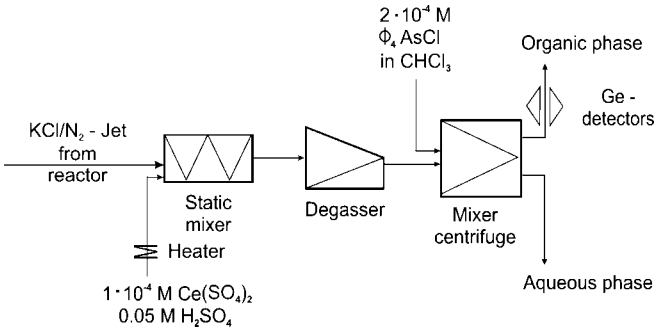

Fig. 3. Flow sheet for the separation of technetium from fission products by solvent extraction using SISAK 3 [62].

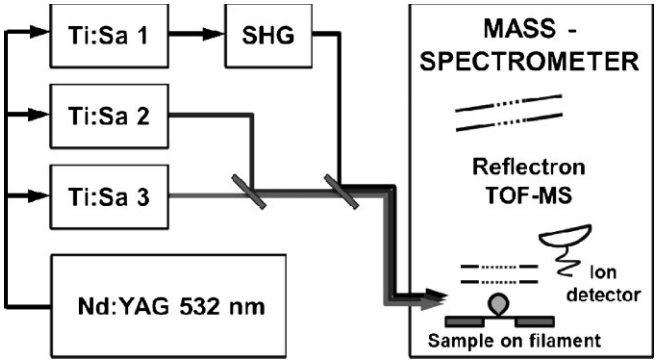

Fig. 4. Set up of the RIMS system with a pulsed Nd:YAG pump laser and three titanium-sapphire lasers, and a time-of-flight mass spectrometer [67].

to the SISAK system and extracted into 0.25 M dibutylphosphoric acid dissolved in toluene. Liquid scintillation counting was applied to register the radiation of Rf-257.

A MicroSISAK system is under development based on a microreactor. The phase separation takes place on hydrophobous Teflon membranes of 0.5–1 μm pore size [64]. The flow rates of the phases are reduced to ∼ 0.2 mL/min which is about two orders of magnitude lower compared to SISAK 3 and extremely important to solve counting problems in the heavy element studies.

2.2 Laser mass spectrometry

2.2.1 Experimental arrangements

In most of the experiments described here RIMS with pulsed laser excitation and time-of-flight mass spectrometry (TOF) has been used. The feature of this approach is a rather large bandwidth of the laser light of usually a few GHz, sufficient for the suppression of atomic and molecular interferences and a medium resolution of the mass spectrometer. For the TOF mass separation process the laser pulse delivers the start signal and the detected photo-ion after a flight path of ∼ 1 m the corresponding stop signal. An atomic beam of the element to be investigated is obtained by resistive heating of a sandwich filament consisting of a thin tantalum backing on which the element is electrolytically deposited (3 mm spot) either after a chemical separation procedure or directly from a pure solution in form of its hydroxide and covered with a thin layer (∼ 1 μm) of titanium or zirconium by sputtering. By heating such a filament the hydroxide is converted to the oxide which is reduced to the metallic state during the diffusion through the covering layer [65]. Efficient release of atoms from the sandwich filaments occurs at temperatures between 800 and 1200 °C. For protactinium an atomic beam could not be produced in this way, neither with titanium and zirconium nor with thorium as reducing agents; therefore an experimental value of the first IP of protactinium with RIMS is still missing.

For the IP measurements of the actinides with the exception of actinium and neptunium a laser system consisting of three dye lasers pumped by two powerful copper vapour lasers (6.5 kHz, 30 ns pulse duration) was used [66], which provides a broad tuning range over the full visible spectral range with a bandwidth of 1.5–6.6 GHz. The dye laser beams are focused by means of quartz fibres or prisms into the apparatus where they cross the atomic beam perpendicularly. The ions produced are accelerated by electric fields and detected with multichannel plate detectors after the passage through a field-free drift tube.

For all other applications of RIMS outlined here a system with a set of three tunable titanium-sapphire (Ti:Sa) lasers simultaneously pumped by a frequency doubled Nd:YAG laser with a repetition rate of 5–10 kHz, as illustrated in Fig. 4, has been used [67]. The pump laser operates at a wavelength of 532 nm and delivers an average laser power of 50–60 W with a pulse duration of 200 ns. Wavelength selection for the Ti:Sa lasers is obtained by a combination of a birefringent filter and an etalon yielding a spectral bandwidth of about 5 GHz. The ∼ 30 ns pulses of the three lasers are temporally synchronized by fast switching of intra-cavity Pockels cells. Wavelength measurements are performed with a commercial wavemeter (ATOS). The operating wavelength of the Ti:Sa lasers can be tuned between 740 and 880 nm with a set of dielectrically coated mirrors and by rotating the birefringent filters. The blue laser light necessary for, *e.g.*, the first excitation step in Pu or Np is produced by second harmonic generation (SHG) of the fundamental radiation of one Ti:Sa laser with a BBO (β-BaB_2O_4) crystal. The outgoing laser beams are transported through an optical fibre and focused to overlap in the interaction zone jointly with the atomic beam.

2.2.2 Excitation/ionization schemes for Pu and Np

The isotope selective ultra trace analysis of Pu by RIMS requires an efficient excitation and ionization scheme. In addition to that the precise transition wavelengths for all isotopes of Pu and the saturation behaviour of each excitation step must be known [67]. In the case of Np only the long-lived isotope Np-237 is of interest for which an effective three-step excitation and ionization scheme had to be explored [68].

For the RIMS measurements on Pu a scheme with $\lambda_1 = 420.76\,\text{nm} \equiv 23\,766\,\text{cm}^{-1}$; $\lambda_2 = 847.28\,\text{nm} \equiv 11\,803\,\text{cm}^{-1}$ and $\lambda_3 = 767.53\,\text{nm} \equiv 13\,029\,\text{cm}^{-1}$ was used, the latter step populating a high lying Rydberg state just a few cm^{-1} below the first ionization potential of plutonium. Therefore, an electric field of 1.5 Vcm^{-1} is sufficient for the ionization. The isotope shifts in this excitation scheme have been measured [67] for the plutonium isotopes 238, 239, 240, 241, 242, and 244 (Table 1) as well as the saturation behaviour.

Table 1. Measured transition wavelengths for the plutonium isotopes ^{238}Pu–^{244}Pu [67].

Isotope	λ_1 (cm^{-1})	λ_2 (cm^{-1})	λ_3 (cm^{-1})
^{238}Pu	23 766.40(2)	11 802.45(2)	13 028.80(2)
^{239}Pu	23 766.32(2)	11 802.52(2)	13 028.80(2)
^{240}Pu	23 766.16(2)	11 802.59(2)	13 028.81(2)
^{241}Pu	23 766.11(4)	11 802.64(4)	13 028.79(4)
^{242}Pu	23 765.98(2)	11 802.72(2)	13 028.81(2)
^{244}Pu	23 765.75(2)	11 802.84(2)	13 028.81(2)

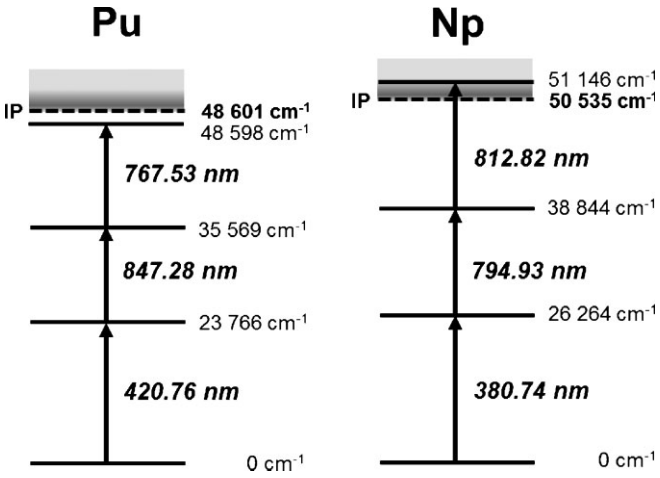

Fig. 5. Resonant excitation/ionization schemes for ultra trace analysis of plutonium and neptunium [*cf*. 67, 68].

These data must be taken into account for exact isotope ratio measurements.

In the studies with Np-237 five different resonance ionization schemes could be investigated and characterized with respect to their saturation behaviour and relative efficiency [68].

The schemes used for ultra trace analysis of Pu and Np are shown in Fig. 5.

2.2.3 Photoionization threshold method

The method applied for the determination of ionization potentials is based on the determination of the photoionization thresholds in the presence of an external electric field [69]. The observed ionization threshold W_{th} depends on the electric field strength as follows:

$$W_{th}(E) = \mathrm{IP} - 2\sqrt{\frac{Z_{eff}e^3}{4\pi\varepsilon_0}}\sqrt{E} = \mathrm{IP} - \mathrm{const}\sqrt{E}$$

where e is the electric charge of the electron, Z_{eff} the effective charge number of the core, ε_0 the permittivity of the vacuum, IP the first ionization potential and E the external electric field. For the determination of the photoionization threshold, a highly excited level of the atom is populated by a two-step or one-step (Ac, Np) resonant excitation. The ionization laser is scanned in the presence of E across the ionization threshold W_{th} which is indicated by a sudden increase of the ion count rate. This procedure is repeated for various electric field strengths and the extrapolation of $W_{th}(E)$ to zero field strength yields the energy of the first ionization potential.

3. Results

3.1 Fast chemical separations

The fast discontinuous and continuous separation methods described here were used in combination with high-resolution gamma-ray and alpha-spectroscopy for the identification of short-lived nuclides and for detailed studies of their decay properties. This will be demonstrated by a few examples.

The discontinuous separation procedure for technetium (Fig. 1) enabled the investigation of the neutron-rich isotopes up to Tc-108. Fig. 6 shows a γ-ray spectrum of a technetium fraction [50] produced by the fission of Pu-239. The γ-rays of 36 s Tc-106, 21 s Tc-107 and 5 s Tc-108 can be identified.

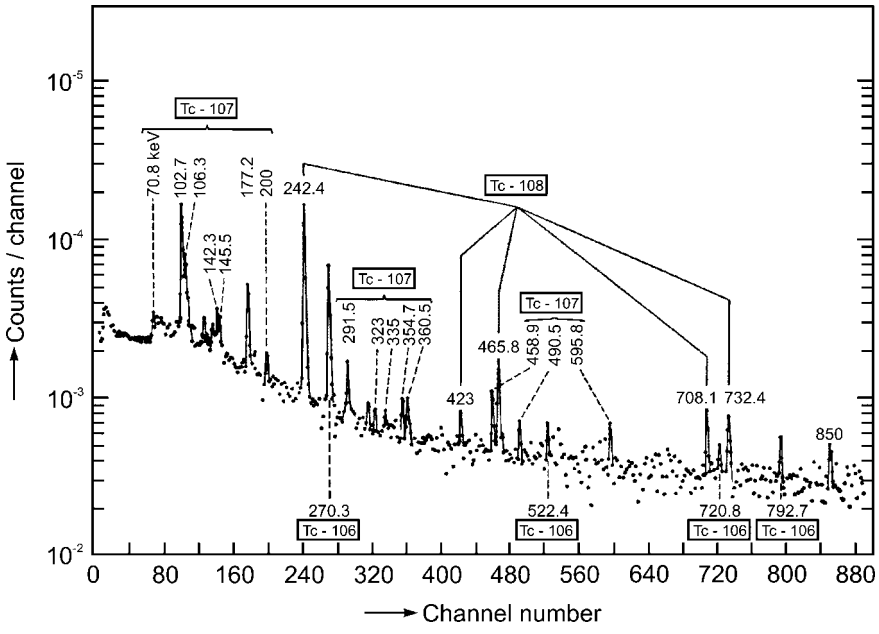

Fig. 6. Gamma-ray spectrum of technetium isotopes produced by fission of Pu-239 measured after fast chemical separation [50].

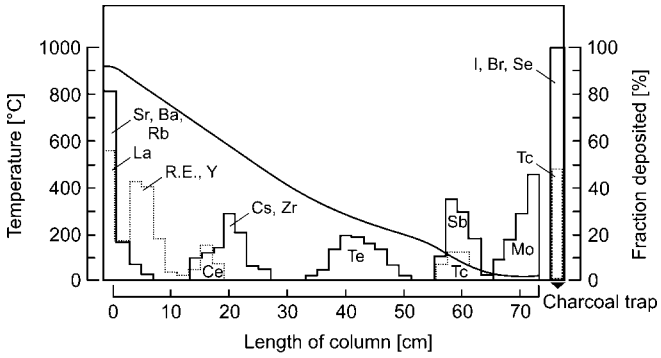

Fig. 7. Element distribution in a thermochromatographic quartz column filled with quartz powder and 7 vol % chlorine as active gas [57]. The temperature gradient along the column is also shown.

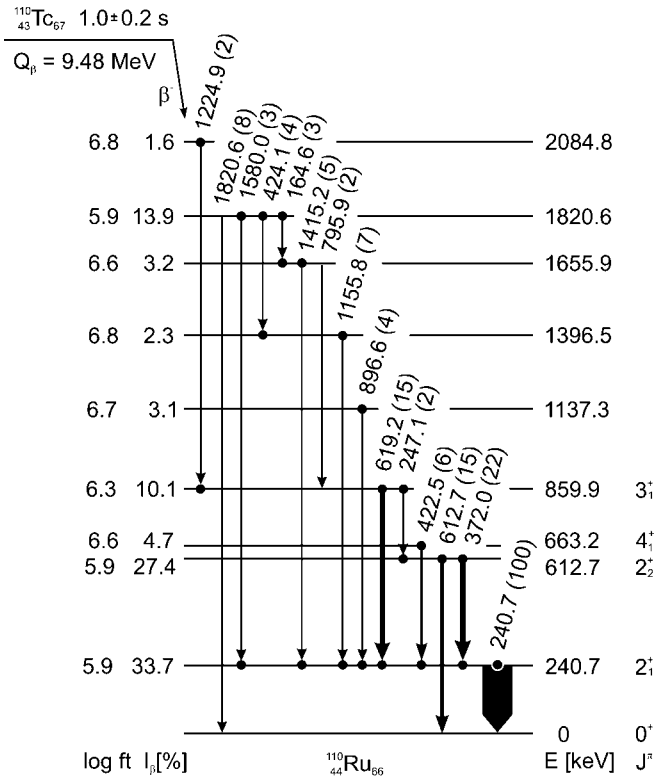

Fig. 8. Level scheme of Ru-110 as obtained by gamma-gamma coincidence measurements in the isolated technetium fraction [62].

Fig. 7 illustrates the element distribution of the neutron-induced fission products of U-235 in the thermochromatographic quartz column with 7 vol % of chlorine in the carrier gas and the arrangement given in Fig. 2 [57].The chlorides of the alkaline, alkaline earth and the lanthanide elements are either non-volatile or only slightly volatile. Zirconium and tellurium are moderately volatile whereas antimony, part of technetium and molybdenum are found in the cold part of the column. Iodine, bromine, selenium, and technetium are collected in the charcoal trap.

With the SISAK 3 separation procedure for technetium (Fig. 3) it was possible to study the levels in Ru-110 *via* the γ-rays following the β^--decay of Tc-110 as shown in Fig. 8, indicating that this isotope belongs to the transitional nuclei [62]. Furthermore, the half-life of Tc-110 could be determined from the decay analysis of the strongest γ-lines of Tc-110 to be 1.0 ± 0.2 s. In the same experiment the β^--decay of 0.9 s Tc-109 has been studied and six γ-lines could be assigned to this nuclide.

3.2 Laser mass spectrometry

3.2.1 Ultra trace analysis and isotope ratio measurements

With the set up shown in Fig. 4 and the excitation/ionization schemes presented in Fig. 5 an overall efficiency of $\sim 3 \times 10^{-5}$ for plutonium and $\sim 10^{-6}$ for neptunium has been obtained as could be shown with calibrated samples of Pu-239 and Np-237 resulting in a limit of detection (LOD) of $\sim 10^6$ atoms (0.4 fg) for plutonium and $\sim 10^7$ atoms (4 fg) for neptunium in a real analytic sample for a single isotope with a signal/noise ratio of 3 and a 3σ-confidence level. The overall efficiency can be explained by the different experimental steps involved: chemical separation ($\sim$ 50%), atomization during evaporation ($\sim$ 50%), ground state population ($\sim$ 40%), spatial overlap of atomic beam and laser beams ($\sim$ 7%), temporal overlap of the beams ($\sim$ 4%); TOF-transmission ($\sim$ 60%), detector efficiency ($\sim$ 30%), efficiency of optical excitation and ionization (10–100%).

Examples for the isotope selective determination of plutonium in two environmental samples are given in Fig. 9. Fig. 9a shows the spectrum of a water sample from the Irish Sea in which the isotopes Pu-238, Pu-239, Pu-240, Pu-241, and Pu-242 could be determined. In Fig. 9b a TOF-spectrum

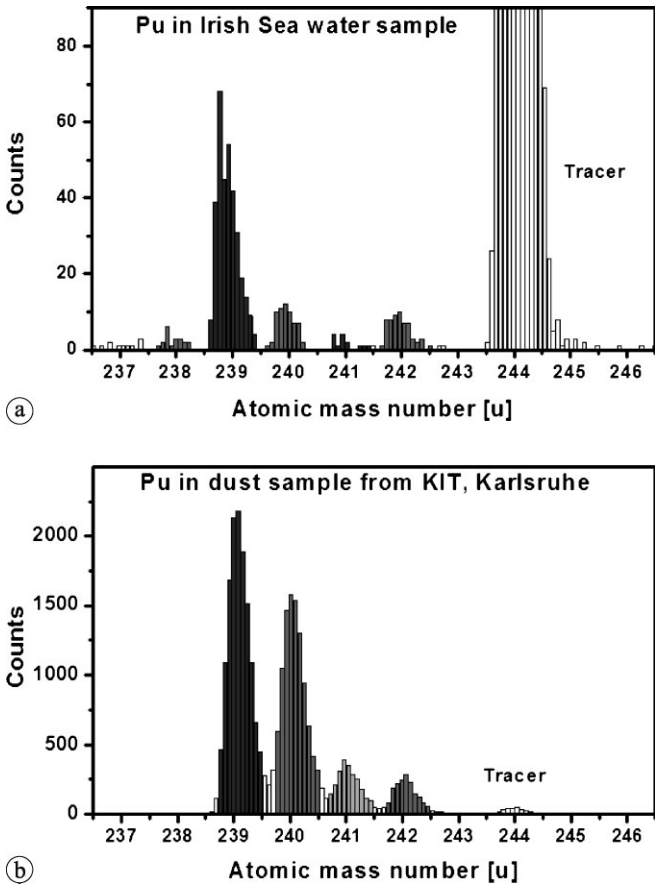

Fig. 9. RIMS-spectra of plutonium for (**a**) a water sample from the Irish Sea and (**b**) a dust sample contaminated with plutonium from the reprocessing plant at KIT.

Table 2. Isotope ratios for plutonium as obtained with RIMS for the NIST standard SRM 996 [67].

Pu isotopes	Measured ratios	Certified ratios
238	0.00004(3)	0.00004(1)
239	0.00039(9)	0.00035(2)
240	0.0065(4)	0.0069(1)
241	0.00054(10)	0.00037(2)
242	0.0137(5)	0.0135(1)
244	1	1

of a dust sample contaminated with plutonium from the reprocessing plant at the Karlsruhe Institute of Technology is presented with isotope ratios typical for reactor plutonium.

It should be mentioned that for all plutonium measurements with RIMS a known amount of Pu-244 tracer is added for quantification prior to the chemical separation in order to correct for variations in the RIMS efficiency and/or the chemical yield. In this case only isotope ratios and no absolute values must be measured to obtain the absolute content of the various plutonium isotopes.

By now ultra trace determination of plutonium with RIMS has become a routine method and is applied regularly for a variety of different environmental samples. The sensitive detection of Np-237 by laser mass spectrometry will be used for diffusion and migration studies in, *e.g.*, clay minerals.

For exact isotope ratio measurements of plutonium the isotope shifts of the individual isotopes (see Table 1) have to be taken into account for the excitation/ionization schemes used. In Table 2 the isotope ratios for the NIST standard SRM 996 as measured with RIMS are summarized. During the measurement the wavelengths of laser one and two were alternately set for each isotope to the correct wavelengths from Pu-238 to Pu-244 whereas the wavelength of the third laser was kept constant. The ratios relative to Pu-244 could be detected over a dynamic range of four orders of magnitude and are in good agreement with the certified values. The slight deviation for the odd-A isotope Pu-241 is ascribed to the influence of the hyperfine-structure and the individual excitation probabilities of different hyperfine-components.

3.2.2 First ionization potentials

The first ionization potentials of Th, U, Np, and Pu were determined very precisely by laser spectroscopy [32, 43–45, 70], among others by studying long-lived Rydberg series converging to one or more limits in the ion. For such measurements gram amounts of material were required which are not available for the heavier actinides and very difficult to handle because of the strong radioactivity. With RIMS the accurate determination of the first IP of the actinides with samples of only 10^{12} atoms ($\sim$ 400 pg) or less could be executed. The photoionization thresholds were determined with electric field strengths of 1.6–340 V cm^{-1}. Table 3 documents the excitation schemes [22, 71, 72] applied for the various actinides. In the case of uranium and berkelium two alternative excitation schemes have been used leading to the same ionization potential. The increase of the signal at the threshold can be determined with an accuracy between 0.5 and 2 cm^{-1}, depending on the counting statistics.

As an example a plot of the measured ionization thresholds *vs.* the square root of the electric field strength E for the elements berkelium, californium, and einsteinium is shown

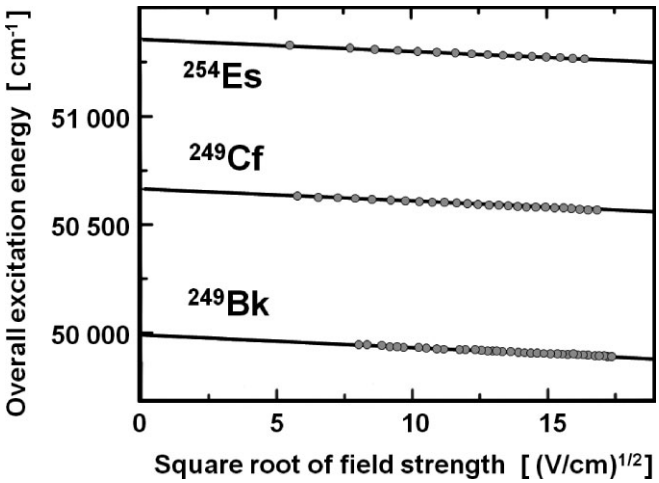

Fig. 10. Plot of the ionization thresholds *vs.* the square root of the electric field strength for Bk, Cf, and Es. The first ionization potential is obtained by extrapolation to zero field strength.

Table 3. Excitation schemes for the determination of the first IP of actinide elements by RIMS. The last step laser wavelength is approximate because the laser is scanned in the presence of an electric field of various voltages [22].

Actinide element	λ_1 (nm) air	First excited state (cm^{-1})	λ_2 (nm) air	Second excited state (cm^{-1})	Ionizing λ (nm)
Ac	388.56	25 729.0	–	–	$\approx$ 568
Th	580.42	17 224.3	622.90	33 273.8	$\approx$ 568
U	639.54	15 631.9	591.47	32 534.1	$\approx$ 577
			585.85	32 696.3	$\approx$ 582
Np	311.81	32 061.3	–	–	$\approx$ 541
Pu	648.89	15 406.6	629.57	31 285.9	$\approx$ 579
Am	640.52	15 608.5	654.41	30 885.1	$\approx$ 578
Cm	655.46	15 252.2	640.56	30 859.1	$\approx$ 573
Bk	565.90	17 666.0	720.50	31 541.3	$\approx$ 544
			664.52	32 710.3	$\approx$ 581
Cf	572.61	17 459.2	625.04	33 453.7	$\approx$ 583
Es	561.53	17 803.5	661.13	32 924.9	$\approx$ 544

Table 4. First IPs (IP_{exp}) of the actinide elements determined by RIMS. Tabulated are also IPs from laser spectroscopy measurements. The method and reference is given in column 5 (RA = comparison of lifetimes of Rydberg and autoionizing states, RC = Rydberg convergence limits). The predictions by extrapolation of spectroscopic data [41] are presented in the last column.

Actinide element	IP_{exp} (cm^{-1}) (RIMS)	IP_{exp} (eV) (RIMS)	IP (cm^{-1}) (others)	Method and references	Extrapolated [41]
Ac	43 398(3)	5.3807(3)			41 700(1000)
Th	50 867(2)	6.3067(2)	50 890(20)	RA [32]	49 000(1000)
Pa	–	–			47 500(1000)
U	49 957(2)	6.1939(2)	49 958(4)	RC [43]	48 800(600)
			49 958.4(5)	[70]	
Np	50 535(2)	6.2655(2)	50 536(4)	RC [44]	49 900(1000)
Pu	48 601(2)	6.0258(2)	48 604(1)	RC [45]	48 890(200)
Am	48 180(3)	5.9736(3)			48 340(80)
Cm	48 324(2)	5.9914(2)			48 560(200)
Bk	49 989(2)	6.1978(2)			50 240(200)
Cf	50 665(2)	6.2817(2)			50 800(200)
Es	51 358(3)	6.3676(3)			51 800(200)

in Fig. 10. As can be seen the experimental values fit very well onto the linear extrapolations to zero field strength which was carried out by least squares fits.

All the first ionization potentials of the actinide elements measured with RIMS are summarized in Table 4 and compared with data from the literature. The uncertainties of the RIMS values are statistical errors given as two standard deviations (2σ) derived from the least squares fits and weighted errors for each data point.

The normalized first ionization potentials of the actinides for the process $5f^N 7s^2 \rightarrow 5f^N 7s$ as evaluated from the RIMS data are lower for the heavier actinide elements compared to the extrapolated data [41] and slightly above the Hartree–Fock calculations [42]. For the lighter actinides, the experimental values for the IPs show strong deviations from the linear dependence which is probably related to the fact that the ground state differs from $f^N s^2$. It is predicted [42] that the actinide IPs should follow the trend for binding energies of the *s*-electrons by forming two straight lines – as in the case of the lanthanides – with a change of slope at americium, the half-filled f-shell. The elements Am to Es confirm this prediction whereas the elements Ac to Pu show considerable scattering.

The determination of the first IP of fermium with $2–5 \times 10^{10}$ atoms of Fm-255 ($T_{1/2} = 20.1$ h) with RIMS failed thus far due to the fact that absolutely no spectroscopic data for fermium were available and due to the rather short half-life of Fm-255. However, with a filament of 2×10^{10} atoms of Fm-255 it was possible to store the Fm-atoms in an argon buffer optical cell and to excite resonantly and finally ionize the atoms with two beams of excimer pumped tunable dye lasers. Two atomic resonances of fermium positioned at 25 099.8(2) cm^{-1} and 25 111.8(2) cm^{-1} could be observed for the first time and their lifetimes were estimated [73].

The extension of the RIMS-method for IP measurements to elements beyond fermium is difficult due to the limited amounts of material available and the short half-lives of transfermium isotopes. Here a technique based on resonance ionization of on-line produced isotopes in an argon buffer cell followed by ion-guide extraction and mass detection of the resonantly ionized atoms may solve this problem [74].

The high precision of RIMS for IP measurements of the actinides could also enable a determination of a predicted isotope dependence of the IP, observable especially easily for uranium and plutonium whose isotopes differ significantly in their neutron number, like U-232 and U-238 or Pu-236 and Pu-244. So far no experimental data have been collected.

Very recently, the first IP of technetium was determined with high accuracy by evaluating Rydberg convergences towards the first ionization potential as well as towards two low-lying excited states of the singly charged technetium ion [46]. For this, Rydberg states of Tc-99g were populated by three step resonance excitation. From the convergence limits a value of IP = 7.119380(32) eV ≡ 57 421.68(26) cm^{-1} for the first ionization potential of technetium could be evaluated, slightly deviating from the data published in the 1950s of 7.23 or 7.28 eV.

4. Conclusions

Fast chemical separation procedures can be widely applied in the field of nuclear research and together with high-resolution radiation spectroscopy represent powerful resources for the investigation of short-lived nuclides. So far, rapid separation procedures have mainly been used for studies of fission products and the transactinide elements. Particular advantages of the chemical methods are selectivity and sensitivity and, due to the high resolution with regard to the atomic number, they allow an unambiguous identification of even a few atoms. Half-life regions down to about one second can be covered with these methods which are close to the limit as determined by diffusion of chemical species through boundary layers between two phases or by the velocity of phase separations. The studies of the chemistry of the heaviest elements whose half-lives get shorter and shorter with increasing atomic number require chemical procedures on a time scale so far not covered. Possibly this problem may be solved by combining specific nuclear effects with selected chemical steps. Therefore, the development of chemical procedures, which can be performed in the millisecond

range, will have to be addressed as research tasks for the future.

Laser mass spectrometry in different experimental arrangements is well suited for ultra trace analysis and isotope ratio measurements of long-lived isotopes, *e.g.*, of plutonium and neptunium. Due to the high selectivity and sensitivity of this technique a detection limit of $\sim 10^6$ atoms results which is important, among others, for migration studies and low-level surveillance of the environment.

The RIMS method is also versatile for the precise determination of the first ionization potential with samples as low as $\sim 10^{12}$ atoms as could be demonstrated for 10 actinide elements so far. The method implies ionization in an electric field with extrapolation to field strength zero. For even heavier elements on-line experiments are necessary in combination with resonance ionization in an argon buffer cell.

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